

A Fiber Optic Reflection-UV/Vis/NIR-System for Non-Destructive Analysis of Art Objects

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Abstract

A fiber optic measuring system for non-destructive pigment analysis using reflection-Ultraviolet/Visible/Near-infrared (UV/Vis/NIR) spectroscopy and its applicability to 19th century watercolor paintings by Moritz M. Daffinger (1790-1849) were presented. The spectra obtained by that system enabled the identification of both organic and inorganic pigments without the risk of damage or contamination of the objects analyzed. Evaluation of the measured spectra was carried out using self-built libraries consisting of reference spectra derived from original 19th century watercolor materials as well as materials of the technical collection of our institute (ISTA). Complementary investigations were carried out with reflection-Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF). These spectroscopic measurements facilitated the evaluation of UV/Vis/NIR spectra and strongly improved the reliability of the results. The results obtained allowed not only the identification of materials but also statements regarding the specific paint technique of the artist.

Keywords

Reflection-UV/Vis/NIR; Fiber Optics; Watercolor Paintings; 19th Century Pigments; Reflection-FTIR; XRF

Introduction

Due to the unique character of many artifacts, material analysis has to be preferably performed in a non-destructive or non-invasive way. Several spectroscopic methods have been used for this purpose, including UV/Vis/NIR, FTIR, Raman and XRF spectroscopy. In the field of art and cultural heritage, non-destructive reflection-UV/Vis/NIR spectroscopy has been applied in various approaches for pigment identification [Rosi et al. (2010); Leona & Winter (2001); Dupuis et al. (2002)] as well as the study of degradation processes [Acquaviva et al. (2010); Koperska et al. (2010); Kampasakali & Varella (2008); Domenech-Carbo et al. (2011)], mainly in combination with other techniques mentioned before. The instrumentation utilized strongly depends on the particular analytical question [Johnston-Feller (2001)]. The literature shows that

materials identification has been carried out using either fiber optics [Miliani et al. (2007); Dupuis & Menu (2006); Elias et al. (2006); Appolonia et al. (2009)] or integration spheres [Bruni et al. (2008); Bonizzoni et al. (2008); Bacci et al. (2009); Sotiropoulou et al. (2008)]. Compared to integration spheres, the main advantage of fiber optics is the possibility to avoid contact to the analyzed surface and thus such devices are frequently employed for the identification of pigments on paintings. Additionally, colorimetric analysis often was performed using hand-held instruments with integration spheres [Acquaviva et al. (2008); Acquaviva et al. (2010); Sotiropoulou et al. (2008)] which enable diffuse illumination of an object. Several measuring geometries have been implemented for fiber optic instruments in order to minimize the contribution of specular reflection, e.g. 0°/45° [Acquaviva et al. (2008); Acquaviva et al. (2010)] or back-scattering configurations with angles of 45° [Rosi et al. (2010); Miliani et al. (2007)] and 22° [Dupuis et al. (2002); Dupuis & Menu (2006); Elias et al. (2006)]. Another important parameter is the spectral range, which can be evaluated, depending on the characteristics of the light source and the range of the detector. In colorimetric analysis, only the visible range (about 380-780 nm) is evaluated usually, whereas for pigment identification also the adjoining UV and NIR regions may provide valuable information. White pigments may be differentiated by their UV absorption and blue pigments by NIR, as Prussian blue and azurite show remarkable absorption beyond 780 nm, whereas cobalt pigments, ultramarine and indigo do not.

In this study, our aim was the identification of pigments on watercolor paintings which show a relatively simple composition compared to other artifacts: paper is used as support and the paint layer consists of the pigments and the binding medium which acts as a protective colloid, usually Arabic gum with minor contents of glycerol and oxgall [Kittel et al.

(1960); Zerr & Rübenkamp (1906); Dörner (2006)]. As the paint layer itself is very thin and translucent in comparison to easel paintings and fine details are encountered frequently on the paintings, analytical techniques with high sensitivity and high spatial resolution are required, as it is the case for reflection-UV/Vis/NIR. In order to meet these requirements, a fiber optic reflection-UV/Vis/NIR system was constructed which allows safe and accurate analysis of the paintings and thus providing information about the materials used by an artist. In addition to the acquired chemical information, the UV/Vis/NIR measurements document the actual visual state (lightness, chroma and hue) at the measuring points of the objects investigated. These data can be used for quantification of color changes in the future due to environmental influences, e.g. light exposure in exhibitions. In addition to UV/Vis/NIR, reflection-FTIR and X-ray fluorescence (XRF) analysis was employed, in order to obtain comprehensive information and to complement the reliability of the results obtained.



FIG. 1 WATERCOLOR PAINTING "PRIMULA VERIS ACAULIS L." BY MORITZ M. DAFFINGER, DATED 1841-1849, 289 x 209 MM², INV. NO. HZ 7662. THE NUMBERS INDICATE MEASURING POINTS 2 AND 3, WHERE BARIUM CHROMATE AND INDIAN YELLOW WERE DETECTED. THE CHARACTERISTIC YELLOW FLUORESCENCE OF INDIAN YELLOW IS SHOWN TOP LEFT

Experimental

Objects

We analyzed 16 watercolor paintings by Moritz M. Daffinger (1790-1849), showing detailed presentations of endemic flowers of the Austrian flora; an example is shown in Figure 1. The paintings depicting a high variety of blue, yellow, green and red hues were selected from 415 objects in the Graphic Collection of

the Academy of Fine Arts Vienna [Jenni et al. (1986)]. All paintings date from the period between 1841 and 1849. In order to obtain additional information about optical properties and the distribution of pigments used for the paintings, near-infrared and UV-fluorescence photographic images were taken and considered for the selection of the measuring points.

Reflection-UV/Vis/NIR

The optical system consists of a 75 W xenon short arc lamp (Ushio Inc., Japan) which is housed in a monochromator (type CLX 75-2 of J&M Analytik AG, Aalen, Germany). Two quartz fiber optic cables (J&M, Aalen, Germany) direct the beam from the source to the measuring point on the object (1250 μ m core diameter, length 2 m) and from the object to the spectrometer (600 μ m core diameter, length 2 m). The utilized spectrometer MSP 400 (J&M) is equipped with a 256 diode array detector which allows measurements in the region from 300-1150 nm.

The fiber optic cables are fixed to a measuring head in 0°/45° geometry by a self-built component which was constructed for a measuring distance of 5 mm between the fiber optics and the object (Figure 2).

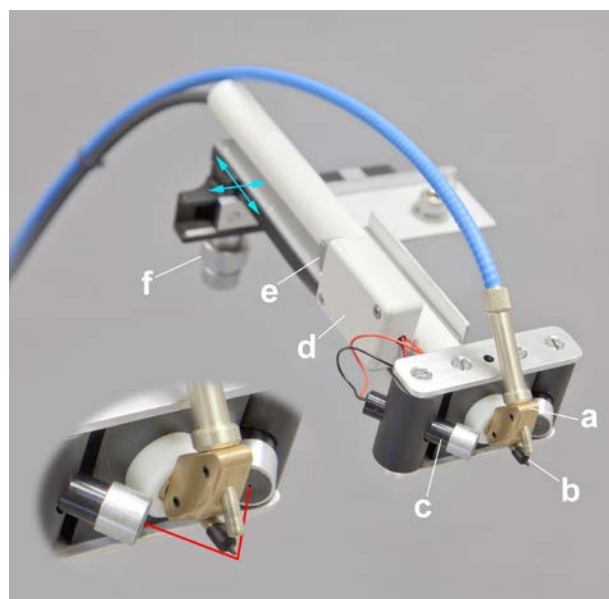


FIG. 2 FIBER OPTIC MEASURING HEAD. MAIN CONSTRUCTION ELEMENTS ARE: 0°/45°-MOUNTING FOR THE QUARTZ FIBER OPTIC CABLES (A), COLLIMATOR MADE FROM LATEX (B), LASER POINTER FOR PRECISE POSITIONING (C), BATTERY COMPARTMENT (D), SWITCH FOR LASERS ON/OFF (E) AND XZ-AXIAL POSITIONING MECHANISM (F). RED LINES SYMBOLIZE THE LASER BEAMS.

The applied measuring geometry ensures that mainly diffusely reflected light reaches the detector [Johnston-Feller (2001)]. The measuring head further is equipped with a xz-axial component (as described by Leona and

Winter (2001) from the mechanical stage of a microscope). That enables a precise linear translation in the two directions perpendicular to each other and can be attached to various positioning devices depending on the particular requirements of the measured objects. Two laser pointing devices are used for precise positioning of the beam as well as control of the correct distance of the fiber optics to the object (Figure 2). The crossing point of the red lasers (672 nm, optical output power less than 1 mW, IMM Meßtechnologie GmbH, Unterschleißheim, Germany) coincides with the beam from the light source in the intended measuring distance of 5 mm from the anterior part of the fiber optic cable to the selected measuring point on the object. In order to prevent light induced damage of the analyzed areas, a collimator was used instead of a focusing lens. Figure 2 shows the pinhole collimator on the fiber optic cable by which a beam diameter of 1.5 mm on the object was achieved. It was manufactured inhouse by dipping an insulin syringe with a 0.3 mm needle (Micro-Fine, Becton Dickinson, Le Pont de Claix, France) in black body painting latex (Beate Uhse AG, Flensburg, Germany) resulting in an aperture of 0.3 mm of the component as well.

The watercolor paintings were analyzed using a positioning device for planar objects with a size of up to 110 x 70 cm² (Figure 3). It consists of two parallel arranged aluminum frames where the object is attached to a plywood panel (covered with a black fabric) in a vertical position. An xy-positioning mechanism with a slidable element was used to move the measuring head.

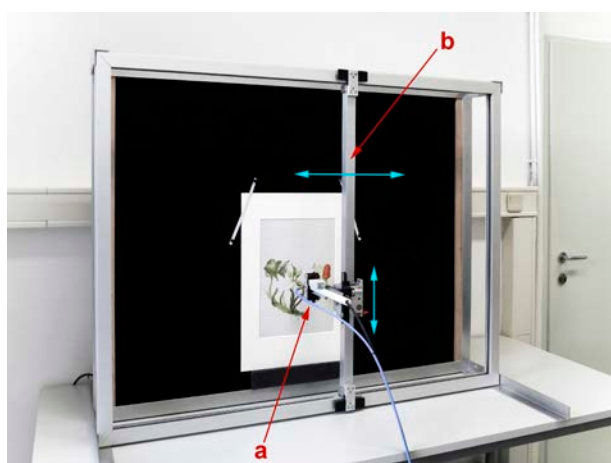


FIG. 3 SELF-DESIGNED AND SELF-BUILT SYSTEM FOR NON-INVASIVE REFLECTION-UV/VIS/NIR SPECTROSCOPY OF PLANAR ART OBJECTS WITH VERTICALLY ADJUSTABLE MEASURING HEAD (A) AND A SLIDABLE ELEMENT MOUNTED ON ROLLER BEARINGS (B).

Reflection spectra were measured in the range of 350-

1000 nm by averaging 3 scans with a total integration time of 2-2.5 seconds relative to both a white standard (J&M) for documentation of the objects and the paper support for the identification of pigments and dyes in order to eliminate a potential influence of the yellowish support (depending on the paint layer characteristics). The dark current was measured and subtracted from each reference and sample measurement. The spectra obtained were evaluated using panorama software (LabCognition, Köln, Germany) and self-built reflection-UV/Vis/NIR libraries. The first derivative of the spectra was calculated as well in order to highlight spectral features.

Reflection-UV/Vis/NIR Libraries

The spectra of the libraries are based on measurements of original 19th century watercolors available in our institute. The watercolors were applied on chromatography paper discs (5 mm diameter, Whatman International Ltd., UK) in various concentrations (0.38, 0.77, 1.53, 3.06, 6.12, 9.18, 12.24 and 15.31 µg pigment per mm²), requiring 1 mg original sample material. Additional pigments not included in the set of the historic materials were used to obtain reference spectra. For this purpose, pigments from the technical collection of our institute were mixed with Arabic gum and applied on paper discs analogous to the historic materials. Reference spectra were collected with a beam diameter of 3 mm by averaging 100 scans with a total integration time of 0.5 seconds.

In addition, several reference spectra were obtained by analyzing small particles (<0.2 mm) from an original paint box of Moritz M. Daffinger (available in the Library of the Academy of Fine Arts Vienna) which were splintered from the watercolor cakes. After identification by use of FTIR microscopy (Spectrum 2000 with microscope i-series, Perkin Elmer, Shelton, CT, USA) on a diamond cell, the particles were spread on wet chromatography paper and measured (after drying) in reflection mode by use of the spectrometer and light source mentioned in the previous chapter coupled to a microscope (Axioplan 2, Zeiss MicroImaging, Jena, Germany).

Reflection-FTIR

Measurements were carried out using a Bruker ALPHA spectrometer with external reflection module (Bruker Optics, Ettlingen, Germany). This accessory utilizes mirrors to direct the beam from the source to the object (spot size ca. 4 mm) and from there to the detector. Spectra were obtained using the average of

64 scans in the region of 375-4000 cm^{-1} with a resolution of 4 cm^{-1} . The measuring geometry is 20°/20° and hence specular reflection usually dominated the appearance of the spectra [Giffiths & de Haseth (2007)]. In order to enable a comparison of the spectra obtained in the reflection mode with spectra of the database used (IRUG - Infrared and Raman Users Group Spectral Database, Edition 2007, Philadelphia, PA, USA; <http://www.irug.org/>), Kramers-Kronig transform was applied to the reflectance spectra resulting in absorption index spectra [Giffiths & de Haseth (2007)]. Systematic investigations carried out on mockups as well as on contemporary acrylic paintings have revealed that this transformation yields more reliable results than a Kubelka-Munk transformation [Vetter & Schreiner (2011)]. Moreover, the materials used for the UV/Vis/NIR library were measured to build up a reflection-FTIR library.

XRF

A self-built system was available for energy dispersive XRF measurements [Desnica & Schreiner (2006)]. It utilizes an Oxford XTF5011 50W-Rhodium x-ray tube (50 kV, 1 mA) and a Röntec XFlash 1000 silicon drift-chamber detector (SDD) with a resolution of 155 eV. X-ray tube and detector are fixed at a 0°/45° geometry. The beam diameter is 1 mm and the spectra are acquired during a measuring time of 100 seconds usually.

Results and Discussion

The results of our analyses demonstrated that high quality reflection-UV/Vis/NIR spectra could be obtained by using the presented measuring system (Figures 4-7, 9 and 10). The utilized positioning device enabled quick and precise operation and thus high measuring rates could be achieved.

With regard to quantitative measurements, the 0°/45° geometry is not an optimal solution because higher deviations from the Kubelka-Munk-theory have been observed for strongly absorbing materials than with other geometries, e.g. diffuse/0° [Kortüm (1969)]. Nevertheless, usable results for a qualitative evaluation of the data can be obtained with this setting and furthermore, only this geometry allows a circular measuring spot for precise illumination of small areas. Due to the narrow beam diameter, the light intensity is relatively weak and alternating ambient light may negatively influence the quality of the spectra. Therefore, spectra are preferably collected in a constant ambient illumination, ideally in a dark room.

This should be considered particularly in case of outdoor UV/Vis/NIR measurements where appreciable variations of lightness may occur in a short time.

The set of pigments identified included cobalt blue, Prussian blue, Gamboge, cadmium yellow, barium yellow, Indian yellow, cochineal, cinnabar and red lead. In general, the evaluation of the obtained spectra was simplified by the fact that only a limited number of pigments were available for artists in the 19th century [Tschelnitz (1857)]. The use of reference spectra with various pigment concentrations was advantageous since concentration dependent shifts of absorption bands could be observed. Identification of earth pigments and ochres by reflection-UV/Vis/NIR was not possible due to the great variety of color shades depending on their provenance and the manufacturing process as well as the lack of characteristic features in their spectra. The applied methods further did not allow the identification of black pigments, it only was possible to exclude carbon black in one case on the painting "Gentiana acaulis L." in consequence of the UV/Vis/NIR spectrum, which showed strong reflection of near infrared radiation on a black area. With respect to these limitations, an additional use of Raman spectroscopy would be highly desirable [Bruni et al. (2008); Bell et al. (1997)].

Table 1 summarizes the results of the reflection-UV/Vis/NIR analysis and complementary reflection-FTIR and XRF measurements.

TABLE 1 EXPERIMENTAL RESULTS

	Cobalt blue	Hookers green	Gamboge	Cadmium yellow	Barium yellow	Indian yellow	Cochineal	Cinnabar	Red lead
r-UV/Vis/NIR	+	+	+	+	+	+	+	+	+
r-FTIR	+	+	+		+	+	+		
XRF	Co	Fe		Cd S	Ba Cr			Hg	Pb

As shown in Figure 4, cobalt blue ($\text{CoO} \cdot \text{Al}_2\text{O}_3$) could be clearly identified from the reflection-UV-Vis/NIR spectrum of a blue measuring point on the painting "Myosotis palustris" and the result was confirmed by reflection-FTIR and XRF detecting cobalt. Furthermore, the spectra measured on the painting show an increasing absorption towards shorter wavelengths (browning) compared to the reference material, which can not be excluded by measuring relative to the paper support. There are several possible explanations for that result: either the artist mixed the hue by intention,

or it results from an alteration of the pigment. Furthermore, the water and/or brush used to apply the blue color may have been contaminated by other colors applied before and thus the browning would result from aspects of the paint technique. As a similar effect could be observed at several other measuring points (e.g. in Figure 6 barium chromate), the last explanation seems to be the most probable.

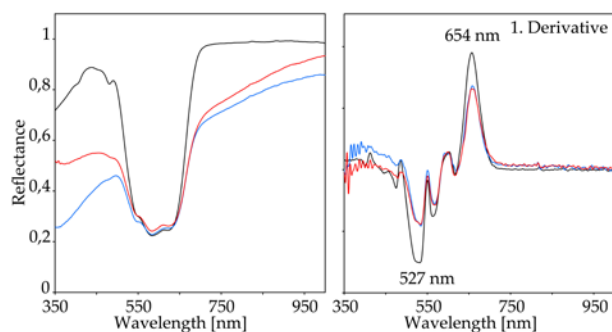


FIG. 4 UV/Vis/NIR SPECTRA OF MEASURING POINT 4 ON THE PAINTING "MYOSOTIS PALUSTRIS" RELATED TO REFERENCE WHITE STANDARD (BLUE), RELATED TO THE PAPER SUPPORT (RED) AND COBALT BLUE (inv. no. 87) OF THE MATERIAL COLLECTION IN OUR INSTITUTE (BLACK).

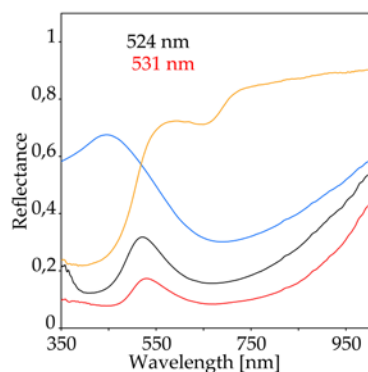


FIG. 5 UV/Vis/NIR SPECTRA OF A GREEN AREA IN THE PAINTING "SOLANUM DULCAMARA L." (RED), HOOKERS GREEN REFERENCE (BLACK), PRUSSIAN BLUE REFERENCE (BLUE) AND GAMBOGE (YELLOW) WHICH WAS IDENTIFIED ON THE PAINTING "GENTIANA ACAULIS L.".

Prussian blue ($\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$) was detected together with Gamboge on several paintings, e.g. "Solanum Dulcamara L." (Figure 5). A mixture of these pigments known under the name Hookers green was available in the mid 19th century. Gamboge is a resinous organic material derived from trees of the family Guttiferae, containing 70-80% resin (xanthonoide constituents, mainly gambogic acid) and 15-25% water-soluble gum [Eastaugh et al. (2008)]. It could not be concluded from our data whether the artist utilized an already blended Hookers green or mixed Prussian blue and Gamboge during the painting process. It was however certain that already blended Hookers green was identified among the original materials of the artist. As depicted in Figure 5, the Hookers green reference from the

original materials of the artist showed a reflection maximum at 524 nm, whereas the correlating maximum of the measured spectrum was slightly shifted to longer wavelengths (531 nm), indicating a comparatively higher content of Gamboge. The identification of Prussian blue and Gamboge was confirmed by reflection-FTIR spectroscopy and Prussian blue also by XRF detecting Fe. In addition to green areas, Gamboge could be determined as well in a yellow area of the watercolor painting "Gentiana acaulis L." by UV/Vis/NIR and reflection-FTIR.

Although the preparation of barium chromate (BaCrO_4) was first described by Vaquelin in 1809, it was first mentioned by Field in 1835 for use as a pigment [Carlyle (2001)]. It is further reported that it was not used commercially as yellow paint in the mid 19th century [Dörner (2006); Eastaugh et al. (2008)]. However, in the yellow parts (measuring point 3 in Figure 1) of the painting "Primula veris acaulis L." barium chromate could be clearly identified. As depicted in Figure 6, the first derivative of the reference reflection-UV/Vis/NIR spectrum showed an inflection point at 434 nm, which was significantly lower than that for most other yellow pigments used in the 19th century and thus characteristic for barium chromate. Even though this inflection point was slightly shifted to 442 nm in the measured spectrum, the presence of barium chromate at this measuring point can be concluded, as the identification of barium chromate could be proved by reflection-FTIR and XRF (detection of Ba and Cr).

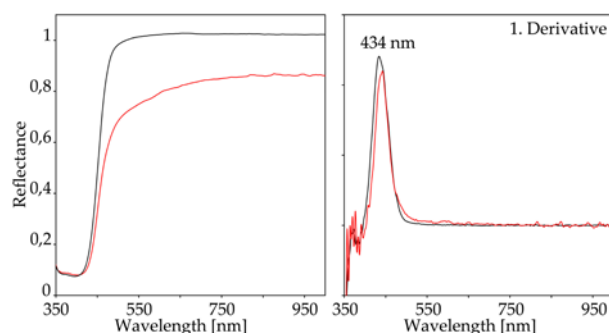


FIG. 6 UV/Vis/NIR SPECTRA FROM MEASURING POINT 3 ON THE PAINTING "PRIMULA VERIS ACAULIS L." IN FIGURE 1 (RED) AND BARIUM CHROMATE REFERENCE FROM THE MATERIAL COLLECTION IN OUR INSTITUTE (BLACK).

In the same painting on measuring point 2 (Figure 1), Indian yellow (magnesium salt of euxanthic acid) [Eastaugh et al. (2008)] could be detected by reflection-UV/Vis/NIR (Figure 7) and reflection-FTIR as the measured spectra were similar to the spectra obtained from an Indian yellow particle which was found in the wallet with watercolor cakes of Moritz Daffinger.

Although barium chromate was identified in addition

to Indian yellow by reflection-FTIR (Figure 8) and XRF at that measuring point, no indication of it could be obtained by reflection-UV/Vis/NIR. From this, it may be concluded that the reflection-UV/Vis/NIR signal from this measuring point mainly originated from a top layer of Indian yellow, whereas also a contribution of barium chromate from subjacent layers (XRF) or surrounding areas (due to the larger spot size of reflection-FTIR) was detected. In fact, the stereomicroscopical investigation as well as the UV-fluorescence image (Figure 1) suggested that Indian yellow was used to overpaint a barium chromate layer.

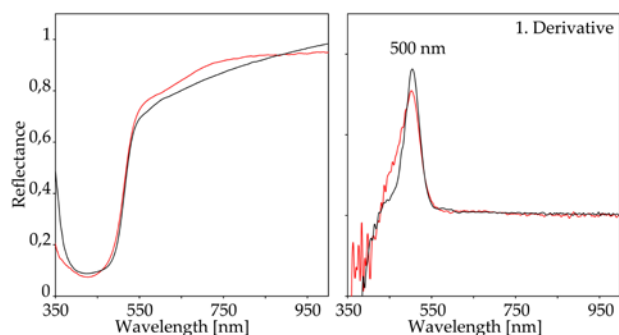


FIG. 7 UV/Vis/NIR SPECTRA FROM MEASURING POINT 2 ON THE PAINTING "PRIMULA VERIS ACAULIS L." IN FIGURE 1 (RED) AND INDIAN YELLOW REFERENCE FROM ORIGINAL PAINT MATERIAL OF THE ARTIST (BLACK).

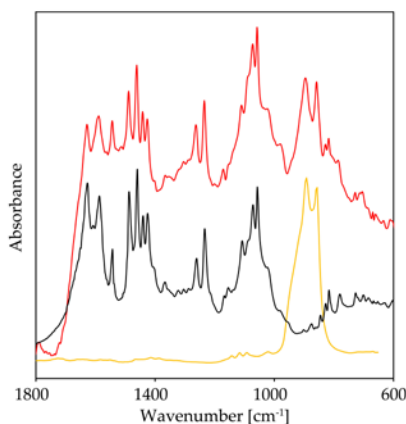


FIG. 8 KRAMERS-KRONIG TRANSFORM OF THE REFLECTION-FTIR SPECTRUM FROM MEASURING POINT 2 ON THE PAINTING "PRIMULA VERIS ACAULIS L." IN FIGURE 1 (RED) VS. INDIAN YELLOW REFERENCE FROM ORIGINAL MATERIAL OF THE ARTIST (BLACK) AND BARIUM CHROMATE REFERENCE IRUG MP0296 (YELLOW) FROM THE IRUG SPECTRAL DATABASE (<http://www.irug.org/>).

Cadmium yellow which was not commercially available until the 1840s [Harley (1982)], could be identified in the painting "Arnica Montana L.", where a spectrum was obtained similar to the reference sample Kremer Pigments, no. 21050. Depending on the manufacturing process cadmium yellow may show a variety of hues [Loya (1988)] and therefore additional analysis with XRF detection of Cd and S was necessary to prove the identification.

Cochineal (carminic acid lake pigment) which mainly was used in form of the alum lake [Tschelnitz (1857)], could be identified by its characteristic UV/Vis/NIR spectrum (Figure 9) as well as by reflection-FTIR on the painting "Sempervivum arachnoideum L.". A confirmation by XRF was not possible since measurements in air do not allow the detection of the elements with low atomic numbers (e.g. C, O and Al). Nevertheless, the XRF results (detection of K, Ca, Pb) support the UV/Vis/NIR-results because cinnabar (HgS), which shows similarities to cochineal in the UV/Vis/NIR spectrum at about 600 nm, could not be detected at the measuring point and can be excluded therefore. Moreover, cochineal was identified in combination with cobalt blue in several paintings (e.g. "Myosotis palustris").

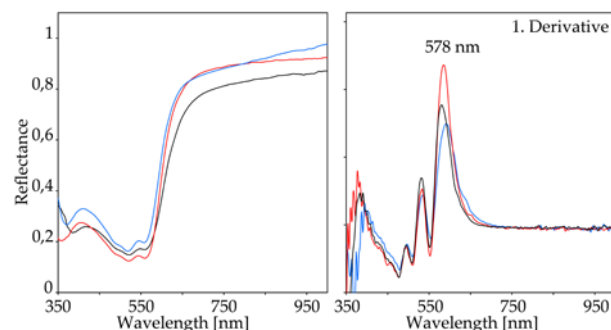


FIG. 9 UV/Vis/NIR SPECTRA FROM A RED MEASURING POINT ON THE PAINTING "SEMPERVIVUM ARACHNOIDEUM L." (RED) VS. COCHINEAL REFERENCE KREMER PIGMENTS, NO. 421008 (BLACK) AND COCHINEAL REFERENCE FROM ORIGINAL PAINT MATERIAL OF THE ARTIST (BLUE).

Cinnabar (HgS) and red lead (Pb₃O₄) were identified on the painting "Physalis Alkekengi L." by reflection-UV/Vis/NIR (similarities to reference spectra of cinnabar of the material collection of ISTA, inv. no. 192, and red lead of ISTA, inv. no. 178) and XRF (detection of Hg and Pb). The first derivative of the reflection-UV/Vis/NIR spectrum (Figure 10) showed an inflection point at 586 nm characteristic for cinnabar and a shoulder at 564 nm characteristic for red lead.

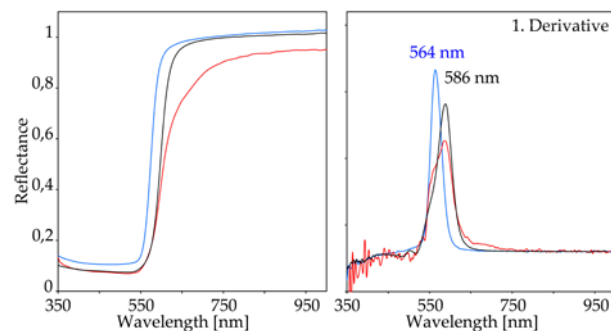


FIG. 10 UV/Vis/NIR SPECTRA FROM A RED MEASURING POINT ON THE PAINTING "PHYSALIS ALKEKENGI L." (RED) vs. CINNABAR REFERENCE ISTA, INV. NO. 192 (BLACK) AND RED LEAD REFERENCE ISTA, INV. NO. 178 (BLUE).

As XRF-detection of Hg and Pb could be interpreted as cinnabar and lead white as well as cinnabar and red lead, this example demonstrated that reflection-UV/Vis/NIR spectroscopy may provide an important contribution to an accurate interpretation, although the spectral features of these red pigments are not overly characteristic. XRF detection of sulfur was not possible due to coincidence of the characteristic peaks of the S K-lines (2.308 keV), Hg M-lines (2.195 keV) and Pb M-lines (2.271 keV). A reflection-FTIR analysis of the paint layer at this measuring point could not be achieved as the spectrum only showed vibration bands characteristic for Arabic gum, derived from a transparent top layer which was applied by the artist in order to achieve an enhanced spatial effect.

Conclusions

The r-UV/Vis/NIR spectra obtained by means of the measuring system presented enable non-destructive, accurate and safe identification of several organic and inorganic historic pigments on 19th century watercolor paintings, especially in combination with complementary non-destructive methods such as reflection-FTIR and XRF. The measuring head allows for easy positioning and is capable to integrate optical fibers of any kind up to 1 cm in diameter, thus the system potentially could be utilized as well for other fiber optic techniques, e.g. FTIR and Raman spectroscopy. The applied minimal sampling techniques for reference materials allow building up spectral libraries from minute samples with almost not visible changes of the materials analyzed.

Furthermore, the results obtained in this work strongly contributed to the knowledge about the paint technique of 19th century artists, documented the actual visual state of the artwork and provided a scientific basis for preventive conservation strategies.

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